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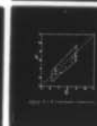
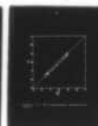
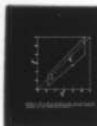
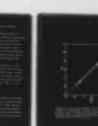
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ON THE GRAM-ATOMIC VOLUMES OF METAL-METALLOID  
GLASS FORMING ALLOYS



By

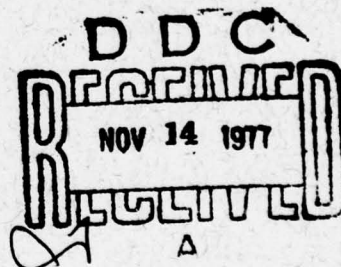
D. Turnbull

Technical Report No. 3

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The gram-atomic volumes, $\bar{V}$ , of several metal(A)-metalloid(B) alloys in their glass or intermetallic crystalline form have been computed from, respectively, density or x-ray diffraction data. It is found that the $\bar{V}$ 's of the silicides and phosphides scale, within $\pm 2\%$ , with the average $\bar{V}$ 's ( $\bar{V}_A^0$ ) of the A elements in their pure f.c.c. states. Actually, for the glassy alloys $\bar{V} \cong \bar{V}_A^0$ within $\pm 2\%$ with the corollary, provided $\bar{V}$ is linear in atom fraction, that $\bar{V}_B \cong \bar{V}_A^0$ within $\pm 10\%$ . This behavior		

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suggests that the topology and scale of the configurations in which the metalloids are sited are determined, within wide limits, by some characteristic spacing in the pure metal host structure. The scaling relation also holds roughly for the germanides and metglasses, but breaks down for some arsenides and  $\text{Fe}_4\text{B}$  glass.

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Division of Applied Sciences

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# ON THE GRAM-ATOMIC VOLUMES OF METAL-METALLOID GLASS FORMING ALLOYS

D. Turnbull

A large number of alloy glasses are composed<sup>1</sup> by combining late transition elements (A) with certain metalloids (B), such as Si, P, C, Ge, B, in ratios ranging roughly from  $A_5B$  to  $A_3B$ . This range usually includes a composition, near  $A_4B$ , at which the system exhibits an extraordinarily deep eutectic.<sup>2,3</sup> The actual glass temperatures,  $T_g$ , vary only slowly with composition around this eutectic;<sup>4</sup> thus, the reduced glass temperature,  $T_{rg} = T_g/T_l$ , where  $T_l$  is the liquidus temperature, will be at or near maximum at the eutectic. The existing thermal measurements indicate that substantial heat is evolved when the alloys form from the pure metallic liquid states of A and B and that considerable short range compositional order develops<sup>5,6</sup> as the alloy melts are cooled to  $T_g$ .

The existing density measurements indicate that the volume changes accompanying the crystallization of alloy glasses are quite small. In particular, Chen et al.<sup>7</sup> found changes of only  $\sim -0.4$  to  $-0.5\%$  in the crystallization of melt quenched Pd-Ni-P glasses and Cargill<sup>8</sup> had reported volume decreases of 0.6 to 1.4% attending the crystallization, to  $Ni_3P+Ni$ , of electrodeposited amorphous Ni-P alloys. Cargill's results also indicated<sup>2</sup> that, within the  $\pm 1\%$  experimental scatter, the partial atomic volume of phosphorus in the amorphous alloys was constant at a value remarkably close, within 2%, to that of Ni over the entire composition range

investigated--  $\text{Ni}_{88}\text{P}_{12}$  to  $\text{Ni}_{74}\text{P}_{26}$ . A similar correspondence holds for crystalline  $\text{Ni}_3\text{P}$ .

This paper reports calculations of the partial atomic volumes of the B elements from density data on A-B metal-metalloid alloys and on the applicability to these results of the correspondence relation indicated for the Ni-P alloys.

### Analysis

Gram atomic volumes,  $\bar{V}$ , of metal-metalloid glasses at  $300^\circ\text{K}$  were calculated from the density data known to me and the specified alloy compositions.  $\bar{V}$  values of the A rich crystalline A-B phases,  $\text{A}_4\text{B}$ ,  $\text{A}_3\text{B}$ , or  $\text{A}_2\text{B}$ , were calculated from the X-ray diffraction data tabulated by Pearson,<sup>9</sup> excepting where otherwise noted. Errors in specifications of the compositions probably contribute uncertainties of at least 1 to 2% to the computed atomic volumes.

The concentration dependence of  $\bar{V}$  for most of the amorphous systems cannot be evaluated precisely because of the narrowness of the composition ranges investigated. In our analysis it is assumed that this dependence is of the form indicated by Cargill's measurements<sup>8</sup> for Ni-P alloys, that is:

$$\bar{V} = X_A \bar{V}_A + (1-X_A) \bar{V}_B \quad . \quad (1)$$

$\bar{V}_A$  values of the pure amorphous A states at  $300^\circ\text{K}$  are generally not available. In our analysis  $\bar{V}_A$  is set equal to  $\bar{V}_A^0$ , the gram atomic volume (or its arithmetic mean if there are two or more A components) of the A element in its  $300^\circ\text{K}$  close-packed crystalline state. This assumption should introduce little error in view of the small volume decreases which



attend crystallization. Thus, we obtain:

$$\bar{V}_B = \frac{\bar{V} - X_A \bar{V}_A^o}{1 - X_A} \quad (2)$$

The results of these calculations are summarized in Table 1. We note for the amorphous combinations of A with either P or Si that  $\bar{V} \cong \bar{V}_A^o$ , to  $\pm 2\%$ , with the corollary that  $\bar{V}_B \cong \bar{V}_A^o$ , to  $\pm 10\%$ . This correspondence would not be especially noteworthy if the  $\bar{V}_A^o$  range between the different alloys were small, as indeed it is in the A-Si alloys investigated, where  $\bar{V}_A^o$  goes from 8.6 to 8.9 while  $\bar{V}_{Si}^o$  ranges between 8.2 and 8.9 cm<sup>3</sup>/gm atom. However, in the A-P alloys  $\bar{V}_A^o$  varies much more widely, from 6.6 to 8.9, as  $\bar{V}_B$  ranges between 6.4 and 9.5. This latter result suggests a volume scaling relation, presumably within certain limits, of  $\bar{V}_B$  to  $\bar{V}_A^o$ .

We see that this same scaling relation seems to extend, with similar variances, to the crystalline silicides and phosphides, in which  $\bar{V}_A^o$  ranges quite widely. For the entire body of results on the phosphides and silicides, whether in amorphous or crystalline form, the ratios of the maximum to the minimum values of the different parameters are as follows:

<u>Alloy</u>	<u>Maximum/Minimum</u>			
	$\bar{V}_A^o$	$\bar{V}_A^o/\bar{V}$	$\bar{V}_B$	$\bar{V}_B/\bar{V}_A^o$
Phosphides	1.35	1.04	1.48	1.21
Silicides	1.57	1.04	1.69	1.18



TABLE 1. Gram atomic volumes ( $\bar{V}$ ) in  $\text{cm}^3/\text{gm. atom}$  of various metal-metalloid alloys in their amorphous solid or crystallized states. In compiling this table, the reviews of Cargill<sup>10</sup> and Davis<sup>12</sup> were used extensively. The gram atomic volumes,  $\bar{V}_A^0$ , of the pure metals were taken from Gschneider's compilation<sup>18</sup> excepting, following Cargill<sup>10</sup>, we have preferred Hume-Rothery's<sup>19</sup> suggested value  $\bar{V}_{\text{Mn}}^0 = 8.77 \text{ cm}^3/\text{gm. atom}$  for manganese. Al was treated as a B element.

Alloy	$\bar{V}$	$\bar{V}_A^0$	$\bar{V}_A^0/\bar{V}$	$\bar{V}_B$	$\bar{V}_B/\bar{V}_A^0$	Ref.
<u>Amorphous Silicides</u>						
$\text{Pd}_4\text{Si}$	8.87	8.88	1.00	8.83	0.99	11
$\text{Pd}_{82.4}\text{Si}_{17.6}$	8.78	8.88	1.01	8.31	0.94	4
$\text{Pd}_{78.4}\text{Cu}_{6.1}\text{Si}_{15.5}$	8.71	8.75	1.00 <sub>5</sub>	8.49	0.97	4
$\text{Pd}_{75.6}\text{Cu}_{5.9}\text{Si}_{18.5}$	8.67	8.75	1.01	8.33	0.95	4
$\text{Pd}_{73.8}\text{Cu}_{5.7}\text{Si}_{20.5}$	8.64	8.75	1.01	8.20	0.94	4
$\text{Pd}_{70.8}\text{Cu}_{14}\text{Si}_{15.2}$	8.57	8.59	1.00	8.46	0.98 <sub>5</sub>	4
$\text{Pd}_{75.8}\text{Cu}_8\text{Si}_{16.2}$	8.67	8.71	1.00 <sub>5</sub>	8.46	0.97	4
$\text{Pd}_{79.5}\text{Ni}_4\text{Si}_{16.5}$	8.74	8.765	1.00	8.62	0.98	12
				$\bar{V}_{\text{Si}}^0 = 9.6$		
<u>Crystalline Silicides</u>						
$\text{Au}_4\text{Si}(\gamma)$ (cubic $\gamma$ )	10.26	10.22	1.00	10.42	1.02	13
$\text{Pd}_3\text{Si}$ (orthorhombic)	8.59	8.88	1.03	7.7	0.87	9
$\text{Pt}_3\text{Si}$ (monoclinic)	8.75	9.09	1.035	7.73	0.85	9
$\text{Ni}_{76}\text{Si}_{24}$ (cubic)	6.49	6.59	1.015	6.17	0.94	9
$\text{Ni}_2\text{Si}$ (orthorhombic)	6.60	6.59	1.00	6.63	1.00 <sub>5</sub>	9
$\text{Co}_2\text{Si}$ (orthorhombic)	6.56 <sub>5</sub>	6.69	1.02	6.32	0.94 <sub>5</sub>	9
				$\bar{V}_{\text{Si}}^0 = 9.6$		

Alloy	$\bar{V}$	$\bar{V}_A^\circ$	$\bar{V}_A^\circ/\bar{V}$	$\bar{V}_B$	$\bar{V}_B/\bar{V}_A^\circ$	Ref.
<u>Amorphous Phosphides</u>						
Ni <sub>81.4</sub> P <sub>18.6</sub>	6.70	6.59	0.98	7.18	1.09	8
Ni <sub>73.8</sub> P <sub>26.2</sub>	6.66	6.59	0.99	6.86	1.04	8
Ni <sub>56</sub> Pd <sub>24</sub> P <sub>20</sub>	7.14	7.28	1.02	6.6	0.91	7
Ni <sub>40</sub> Pd <sub>40</sub> P <sub>20</sub>	7.63	7.73 <sub>5</sub>	1.01	7.20	0.93	7
Ni <sub>16</sub> Pd <sub>64</sub> P <sub>20</sub>	8.32	8.42	1.01	7.92	0.94	7
Co <sub>81</sub> P <sub>19</sub>	6.74	6.69	0.99	6.94	1.04	14
Co <sub>76.4</sub> P <sub>23.6</sub>	6.63	6.69	1.01	6.44	0.96	14
Ni <sub>15</sub> Pt <sub>60</sub> P <sub>25</sub>	8.52	8.59	1.01	8.32	0.97	7
Pd <sub>58.8</sub> Mn <sub>25.2</sub> P <sub>16</sub>	8.95	8.85	0.99	9.50	1.07	15
Pd <sub>51.9</sub> Mn <sub>22.1</sub> P <sub>26</sub>	8.87	8.85	1.00	8.95	1.01	15
Pd <sub>51.9</sub> Mn <sub>22.1</sub> P <sub>26</sub>	8.78	8.85	1.01	8.54	0.96 <sub>5</sub>	15
Pd <sub>65.5</sub> Mn <sub>11.5</sub> P <sub>23</sub>	8.66	8.85	1.02	8.12	0.92	15
Pd <sub>57.8</sub> Mn <sub>19.2</sub> P <sub>23</sub>	8.75	8.86	1.01	8.39	0.95	15
Pd <sub>47.7</sub> Mn <sub>29.3</sub> P <sub>23</sub>	8.78	8.85	1.01	8.54	0.96	15
	8.80	8.84	1.00 <sub>5</sub>	8.65	0.98	15
				$\bar{V}_B^\circ=7.1$		

<u>Crystalline Phosphides</u>						
Ni <sub>3</sub> P (tetragonal)	6.63	6.59	0.995	6.76	1.03	9
Fe <sub>3</sub> P tetragonal	6.96 <sub>5</sub>	7.09	1.02	6.58	0.93	9
Pd <sub>3</sub> P (orthorhombic)	8.66	8.88	1.02	8.00	0.90	9
Co <sub>2</sub> P (orthorhombic)	6.59	6.69	1.00	6.39	0.96	9
				$\bar{V}_B^\circ=7.1$		

Alloy	$\bar{V}$	$\bar{V}_A^\circ$	$\bar{V}_A^\circ/\bar{V}$	$\bar{V}_B$	$\bar{V}_B/\bar{V}_A^\circ$	Ref.
<u>Other Amorphous Phases</u>						
Au <sub>77.8</sub> Ge <sub>13.7</sub> Si <sub>8.5</sub> (liquid at 402°C)	10.95	10.87 <sup>(l)</sup> (402°C)	0.99	11.23	1.04(402°C)	16
Fe <sub>75</sub> P <sub>15</sub> C <sub>10</sub>	6.87	7.09	1.03	6.48	0.91	12
Fe <sub>80</sub> P <sub>13</sub> C <sub>7</sub>	7.08	7.09	1.00	7.1	1.00	17
Ni <sub>75</sub> P <sub>16</sub> B <sub>6</sub> Al <sub>3</sub>	6.57	6.59	1.00	6.53	0.99	12
Ni <sub>49</sub> Fe <sub>29</sub> P <sub>14</sub> B <sub>6</sub> Si <sub>2</sub>	6.73	6.78	1.01	6.78	0.97	12
Ni <sub>39</sub> Fe <sub>38</sub> P <sub>14</sub> B <sub>6</sub> Al <sub>3</sub>	6.56	6.84	1.04	5.66	0.83	12
Ni <sub>36</sub> Fe <sub>32</sub> Cr <sub>14</sub> P <sub>12</sub> B <sub>6</sub>	6.79	6.92	1.02	6.24	0.90	12
Fe <sub>73</sub> P <sub>16</sub> B <sub>6</sub> Al <sub>3</sub>	6.80	7.09	1.04	5.97	0.84	12
Fe <sub>80</sub> B <sub>20</sub>	6.32	7.09	1.12	3.6	0.51	12

Crystalline Germanides

Co <sub>1.76</sub> Ge	6.75	6.69	0.99	6.87	1.03	9
Fe <sub>1.67</sub> Ge	7.07 <sub>5</sub>	7.09	1.00	7.05	0.99 <sub>5</sub>	9
Ni <sub>3</sub> Ge	6.84	6.59	0.96	7.60	1.15	9
Pd <sub>2</sub> Ge	8.75	8.88	1.01 <sub>5</sub>	8.49	0.96	9
Pt <sub>2</sub> Ge	9.14	9.09	0.99	9.24	1.02	9

$$\bar{V}_B^\circ = 12.0$$



The dependence of  $\bar{V}$  and  $\bar{V}_B$  on  $\bar{V}_A^0$  in these alloys is displayed graphically in Figures 1 and 2.

The tendency of  $\bar{V}_B$  to scale with  $\bar{V}_A^0$  persists in certain A-B alloys containing two or more B elements, e.g., molten  $\text{Au}_{77.8}\text{Ge}_{13.7}\text{Si}_{8.5}$  at  $402^\circ\text{C}$ , amorphous  $\text{Fe}_{25}\text{P}_{15}\text{C}_{10}$  and  $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ , and most of the Allied Chemical Metglasses. That the scaling has its limits is shown by the results that the computed gram atomic volume of boron in  $\text{Fe}_4\text{B}$  is only  $(1/2)\bar{V}_{\text{Fe}}^0$ , and that  $\bar{V}_B/\bar{V}_A^0$  is well below 0.9 in some of the other Metglasses containing substantial boron. Also, while the scaling holds for the crystalline A-germanides, there are rather large excesses of  $\bar{V}_B$  over  $\bar{V}_A^0$  for certain crystalline A-arsenides.

Certain alloys of late with early transition metals, e.g., Cu-Zr, constitute another important group of metallic glasses.<sup>20</sup> Density data on Cu-Zr alloys provide no suggestion of  $\bar{V}_{\text{Zr}}$  vs.  $\bar{V}_{\text{Cu}}^0$  scaling. Actually, the calculated  $\bar{V}$ 's of these glasses,<sup>21</sup> as well as of crystalline  $\text{CuZr}_2$ , are simply, within the experimental uncertainty, the averages of the gram atomic volumes of the pure crystalline constituents,  $\bar{V}_{\text{Cu}}^0 = 7.1$  and  $\bar{V}_{\text{Zr}}^0 = 14.04 \text{ cm}^3/\text{gm atom}$ .

### Interpretation of Results

The X-ray diffraction data on metal-metalloid glasses are generally consistent with a model in which the A atoms are in a somewhat relaxed Bernal dense random packed (DRP) arrangement.<sup>10</sup> Polk<sup>22</sup> suggested that the B atoms in these glasses may be sited, with some distortions, in the larger holes formed by the A-DRP structure since they would then be in positions quite similar in environment to those in which they occur

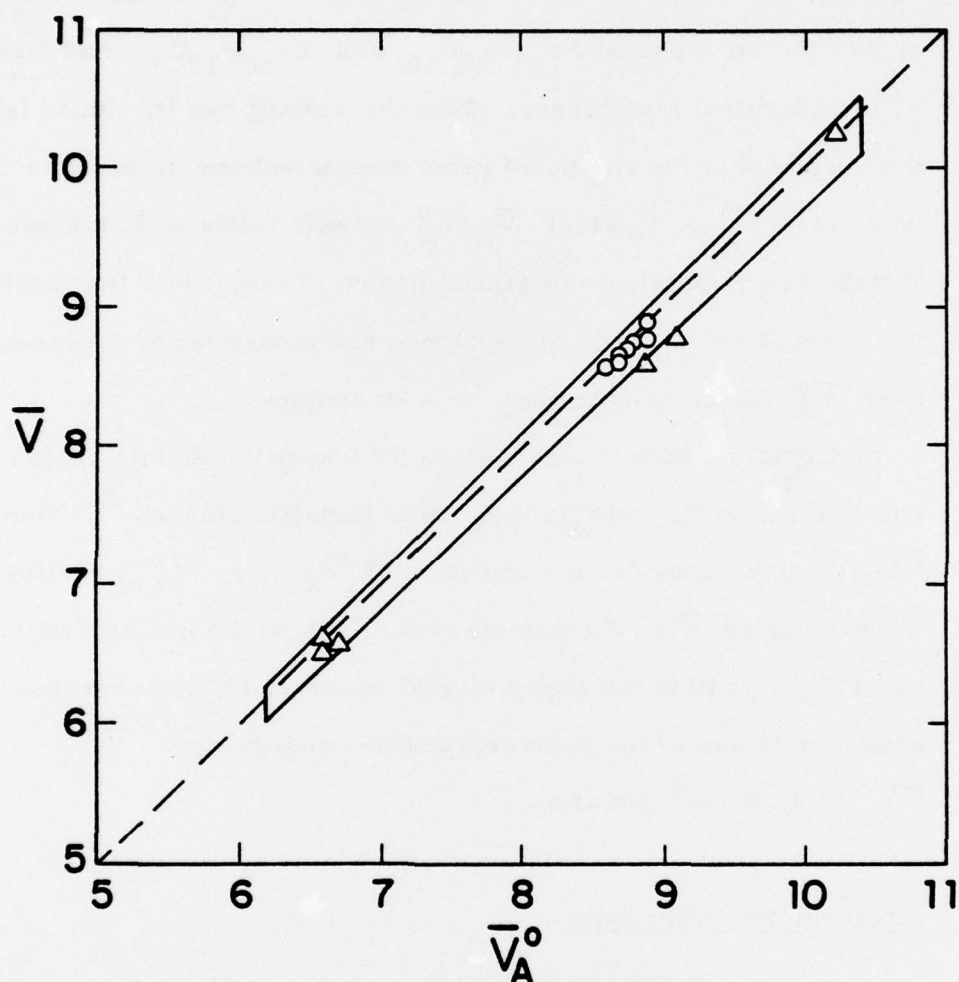


FIGURE 1a. Gram-atomic volumes,  $\bar{V}$  ( $\text{cm}^3/\text{gm. atom}$ ), of metal-silicides vs. the gram atomic volumes,  $\bar{V}_A^0$ , of the pure metal crystals at 300°K.  $\circ$  and  $\Delta$  denote results on, respectively, glass and crystalline alloys. The points are enclosed in an area indicating the estimated,  $\pm 2\%$ , maximum experimental uncertainty range. The dashed line represents the  $\bar{V} = \bar{V}_A^0$  relation.

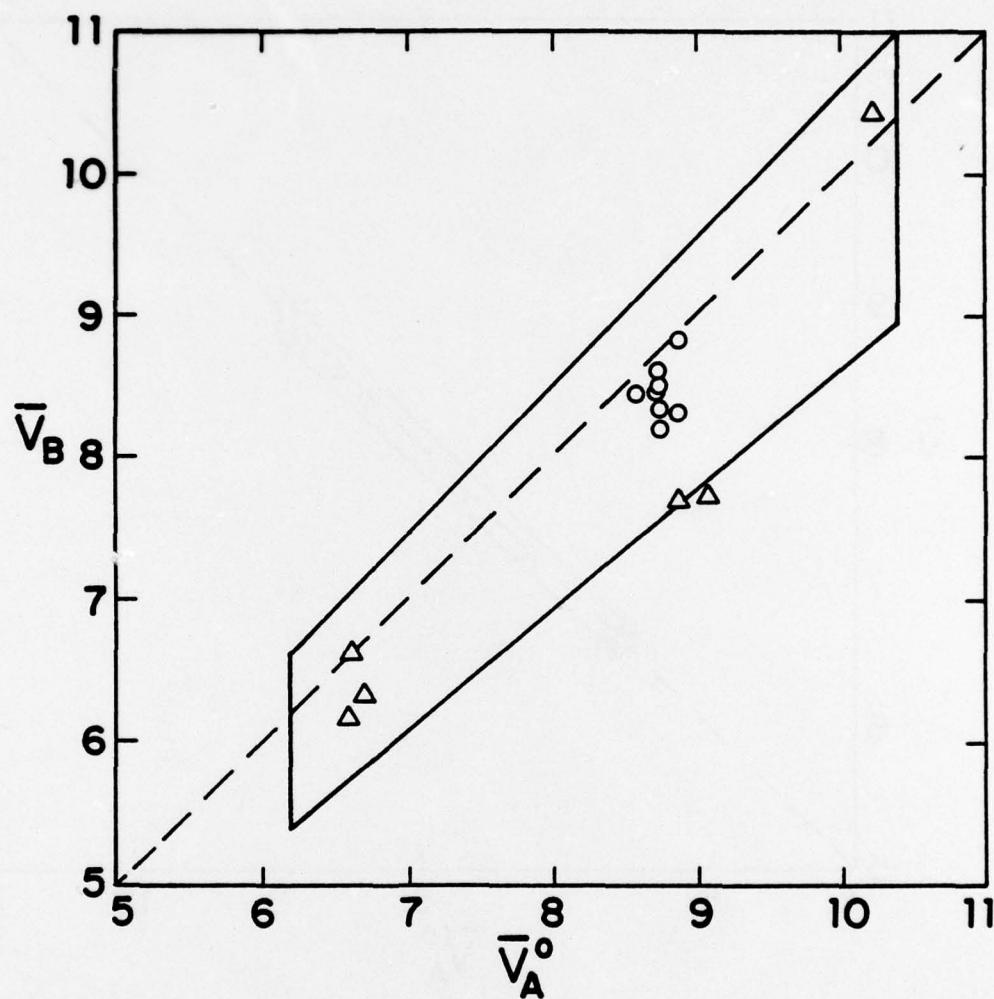


FIGURE 1b.  $\bar{V}_B$  vs.  $\bar{V}_A^o$  for the metal silicides. Enclosed area indicates estimated,  $\pm 10\%$ , maximum experimental uncertainty range. Dashed line represents  $\bar{V}_B = \bar{V}_A^o$ . Symbols are as in Part a.



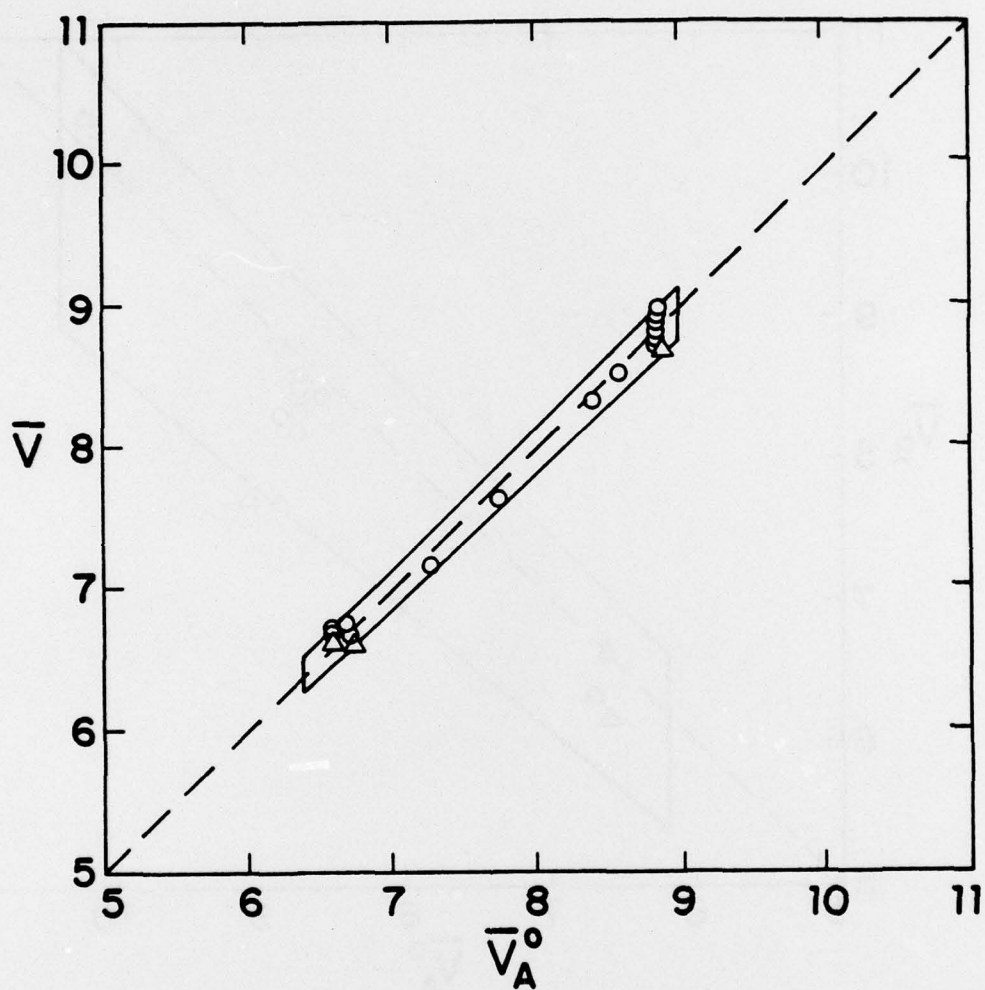


FIGURE 2a.  $\bar{V}$  vs.  $\bar{V}_A^o$  for metal phosphides. Designations are as in Fig. 1a.

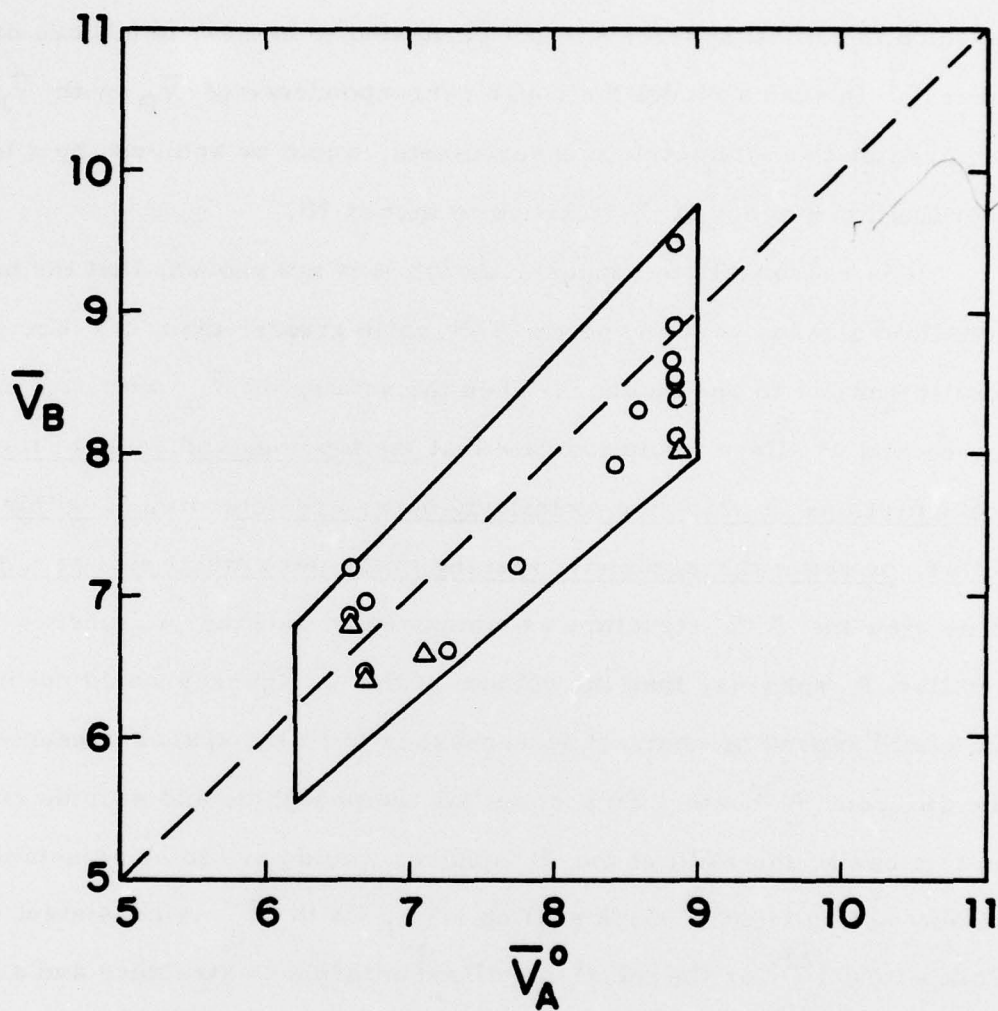


FIGURE 2b.  $\bar{V}_B$  vs.  $\bar{V}_A^0$  for metal phosphides. Designations are as in Fig. 1b.

in certain of the  $A_3B$  crystal structures. Such siting would require AB spacings well below the minimum for AA. Actually, the diffraction data indicate that the structure of amorphous Ni-P alloys is consistent with a two size, radius ratio  $r_P/r_{Ni}$  of  $\sim 0.8$ , hard sphere packing model in which the small spheres are not permitted to be near neighbors of each other.<sup>23</sup> In such a model the rough correspondence of  $\bar{V}_P$  with  $\bar{V}_{Ni}$ , required by the volumetric measurements, would be achieved by a lower coordination number of P relative to that of Ni.

It is reasonable to suppose, though it is not proven, that the metal-metalloid glasses with any given A/B ratio greater than 2/1 are structurally similar to one another. Then the scaling of  $\bar{V}_B$  with  $\bar{V}_A^0$  noted for Si and P alloys would indicate that the topology and scale of the configurations in which the metalloids occur are determined, within wide limits, by some characteristic spacing in the pure metal host structure. If we view the A-B structure as composed by packing A spheres with smaller B spheres, then the volume of the B spheres would not be fixed but would expand or contract as necessary to fit the spaces presented by the different A hosts. To account for the phosphide and silicide results on this basis, the radii of the B spheres would have to be adjustable by amounts of 15 to 20%. Such scaling of  $\bar{V}_B$  with  $\bar{V}_A^0$  is consistent with Polk's model<sup>22</sup> for the metal-metalloid amorphous structure and also with the author's suggestion<sup>2</sup> that the energy of AB type alloys at constant electron density is relatively insensitive to the near neighbor spacings of AB pairs.

It seems that some criterion for the breakdown of the scaling relation, evident from the results on the borides and arsenides, might



be framed in terms of the gram-atomic volume,  $\bar{V}_B^0$ , of the metalloid in its pure metallic state. However, the present results are not adequate for establishing such a criterion. Table 1 lists values of  $\bar{V}_B^0$  at 300°K estimated for Si and Ge by extrapolation, using a thermal expansion coefficient of  $10^{-4}/^{\circ}\text{C}$ , of the specific volumes of their molten states, which are metallic. Also listed is the metallic volume of phosphorus computed from the Goldschmidt radius for this element recommended by Hansen.<sup>24</sup>  $\bar{V}_P^0$  and  $\bar{V}_{Si}^0$  fall within, while  $\bar{V}_{Ge}^0$  is somewhat above, the range of  $\bar{V}_A^0$  of the late transition metal glass formers. Presumably,  $\bar{V}_{Boron}^0$  is far below and  $\bar{V}_{As}^0$  is well above this range.

We have noted that the diffraction and thermal data indicate a high degree of compositional short range order (C-SRO) in metal-metalloid glasses. The temperature dependence of the heat capacity of these alloys suggests that much of the C-SRO develops as the melts are cooled from relatively high temperature to  $T_g$ . It seems reasonable to suppose that the changing degree of C-SRO with  $T$  would contribute substantially to the thermal expansion coefficient,  $\alpha$ , of the molten alloy. The measurements of Chen et al.<sup>7</sup> indicate that the  $\alpha$ 's of Pd-Ni-P alloys increase by factors of at least 1.7 to 2.5 in the glass  $\rightarrow$  melt transition. Whether the  $\alpha$  levels reached by the alloy melts are significantly higher than those of the pure molten metals is unclear since measurements of the latter, especially into the undercooled range, are sparse. The thermal contraction of the alloys to  $T_g$  is evidently sufficient to reduce the volume changes upon crystallization to levels of order  $\sim 1/10$  of those which accompany the crystallization of pure metal melts at  $T_m$ . The free volume model relates the increased atom transport resistance with decreasing  $T$  to

thermal contraction and it was the basis for Ramachandrarao et al.'s<sup>25</sup> recent interpretation for the viscosity behavior of molten glass forming alloys.

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